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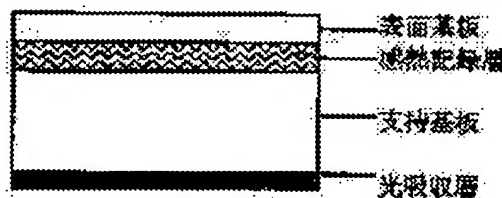
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## (54) METHOD AND APPARATUS FOR RECORDING MULTICOLOR IMAGE

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a method and an apparatus for recording a multicolor image of two or more colors including a color having a short wavelength even without realizing a large cooling speed by using a cholesteric liquid crystal compound.

SOLUTION: A heat-sensitive recording layer containing a thermotropic liquid crystal compound for forming a cholesteric liquid crystal compound is provided between two transparent substrates. In this case, after the recording layer is heated to a temperature exhibiting an isotropic phase or the cholesteric liquid crystal, the layer is cooled at a specific cooling speed. Thus, a cholesteric glass phase is formed. An area of the heat-sensitive recording layer of a recording material exhibiting a selected reflecting color caused by a spiral molecular arrangement is heated and cooled and an image of a first selected reflecting color is recorded, and a pressing force is applied to the area of the image of the first selected reflecting color, thereby color changing to a second selected reflecting color.



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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the multi-colored picture image record approach in which a multicolor display is possible, and multi-colored picture image equipment by the easy approach especially about the image recording approach and equipment to the reversible record medium which used the cholesteric-liquid-crystal nature ingredient.

[0002]

[Description of the Prior Art] a rewritable thermal recording medium (JP,5-69672,A, JP,6-273707,A) -- in case this approach heats the whole record layer to the record laying temperature more than glass transition temperature below with isotropic phase transition temperature, changes it suitably into the liquid crystal condition of a color and cools this below to glass transition temperature, it is the approach of fixing this liquid crystal condition by adjusting the pressure at the time of making it insert in between application-of-pressure means, for example, the heating roller of a couple.

[0003] A cholesteric polymer liquid crystal can fix the cholesteric reflected color at a room temperature by quenching the liquid crystal condition which appeared according to temperature up below to glass transition temperature (T<sub>g</sub>). At this time, the electrochromatic display condition of various color tones can be set up by the difference in that record laying temperature. Moreover, a color tone is determined by the share added at the time of heating. This cholesteric polymer liquid crystal is heated more than isotropic phase transition temperature, a record image can be eliminated by changing a record layer into a transparence condition and quenching it, and reversible record is possible. However, in the case of the polymer liquid crystal system, the technical problem that comparatively long time amount was required for record or elimination actuation occurred.

[0004] The record medium which can be repeatedly written in by quenching the record ingredient with which molecular weight consists of an ingredient with which glass transition temperature contains a cholesteric-liquid-crystal compound or this compound 35 degrees C or more or less by 2000 from a cholesteric-liquid-crystal phase condition if the reflected color of a cholesteric-liquid-crystal phase condition can be saved in ordinary temperature for a long time, and it reheats and it returns to a liquid crystal phase condition is known.

[0005] For example, when 10 and 12-TOKOSA gene dione acid dicholesteryl are quenched from the temperature of 87 to 115 degree C which shows a cholesteric-liquid-crystal phase to 0 degree C, they are fixed to the solid state (it is called a cholesteric glass phase) which shows a cholesteric reflected color. The cholesteric reflected color fixed by changing the temperature which starts cooling changed from blue even to red continuously, and the color was stable more than half a year at the room temperature. Moreover, it was also possible to have fixed another cholesteric reflected color by a cholesteric reflected color disappearing by heating at 119 degrees C or more, and quenching from still more nearly another cholesteric-liquid-crystal temperature (N. Tamaoki, A.V.Parfenov, A.Masaki,

H.Matsuda, Adv.Mater. 1997, 9, 1102 -1104).

[0006] Since this record ingredient is a molecule and it can perform record and elimination actuation in a short time while [ so-called ] molecular weight is or less 2000 extent, rewritable full color record and the application to a multiple-value archive medium are possible for said record ingredient.

[0007] Although the inside molecule cholesteric-liquid-crystal system record ingredient of the above has the description promising as a full color reversible record ingredient, in order to carry out cooling solidification of the cholesteric-liquid-crystal phase at a cholesteric glass phase, it needs to realize a comparatively big cooling rate. In order to fix the selective reflection color it is especially indicated by the elevated-temperature side that is blue, the point which needs a big cooling rate especially poses a problem. Therefore, in a cooling system like usual thermal head equipment, it is difficult to record blue and the special cooling means needed to be added.

[0008]

[Problem(s) to be Solved by the Invention] In the image recording approach and image recording equipment which used the cholesteric-liquid-crystal compound, even if this invention does not realize a big cooling rate, especially, they are the image recording approach and image recording equipment which can record the color of short wavelength, and an easy approach, and aims at offering the approach and equipment which record the multi-colored picture image more than the two color containing the color of short wavelength.

[0009]

[Means for Solving the Problem] this invention persons were able to discover the new phenomenon in which the selective reflection color which recorded first the cholesteric glass phase recorded once by performing suitable pressure treatment under temperature conditions sufficiently lower than the usual record temperature changed to the color by the side of short wavelength, and were able to hit on an idea to this invention.

[0010] When it passes beyond predetermined time amount after record actuation of a selective reflection color, it stops discovering said color change phenomenon. Moreover, the predetermined time amount [ a color change phenomenon ] no longer discovering changes with the storage temperature of the heat-sensitive recording layer from after record actuation termination. as [ be / when thrust at the time of pressure treatment is made small / furthermore, / green ] -- comparatively -- a long wave -- it changes to the color by the side of merit.

[0011] Change of the reflectance spectrum by temperature and the pressure is shown in drawing 2 . a film-like sample -- using -- spectrum measurement -- a spectrum -- colorimetry concentration meter X-Rite938 -- \*\* The \*\* was carried out. The red shown as the thin continuous line in drawing changed to the blue and green which were shown by the thick line by color conversion actuation later explained to a detail. Moreover, the broken line showed the blue result in the record approach which needs the conventional big quenching conditions as a comparison.

[0012] If the mechanism of said phenomenon is clear, there is nothing, but since the cholesteric glass phase immediately after record carried out the short wavelength shift by the effectiveness as the angle-of-visibility dependency of a selective reflection color that it is the same since the spiral pitch became short, and it short-wavelength-ized not by the condition fixed by stability but by the share stress by thrust or the screw axis of a domain inclined, it is considered.

[0013] The first of this invention, based on the above knowledge, at least one side has a heat-sensitive recording layer containing the thermotropic liquid crystal nature compound which forms a cholesteric-liquid-crystal phase between two transparent substrates, and is constituted. After heating said record layer to the temperature which shows an isotropic phase or a cholesteric-liquid-crystal phase, and by cooling with a specific cooling rate The cholesteric glass phase which solidified the spiral molecular arrangement of a cholesteric-liquid-crystal phase is made to form. A part of heat-sensitive recording layer of the record ingredient which can record the image in which the selective reflection color resulting from spiral molecular arrangement is shown Or after heating and cooling all fields with

heating and a cooling means and recording the image of the first selective reflection color, In the predetermined time amount which can carry out color conversion, in the image of the second selective reflection color by applying thrust to the image of the selective reflection color of this first It is in having solved said technical problem by providing the second selective reflection color with the multi-colored picture image record approach characterized by carrying out color conversion by applying thrust to some images of said first selective reflection color, or all fields.

[0014] Furthermore, based on the above knowledge, the second of this invention has a heat-sensitive recording layer containing the thermotropic liquid crystal nature compound with which at least one side forms a cholesteric-liquid-crystal phase between two transparent substrates, and is constituted. After heating this record layer to the temperature which shows an isotropic phase or a cholesteric-liquid-crystal phase, and by cooling with a specific cooling rate The cholesteric glass phase which solidified the spiral molecular arrangement of a cholesteric-liquid-crystal phase is made to form. A means to convey the record ingredient which can record the image in which the selective reflection color resulting from spiral molecular arrangement is shown, The first heating means which heats the record layer part or all the fields of a record ingredient to the temperature which shows an isotropic phase or a cholesteric-liquid-crystal phase, A cooling means to record the image of the first selective reflection color by cooling the record layer which shows said isotropic phase or a cholesteric-liquid-crystal phase with a specific cooling rate, Some images of said first selective reflection color, or a press means to apply thrust to all fields, In the second selective reflection color so that the image of said first selective reflection color may carry out color conversion by the press by said press means And said first heating means, It is in having solved said technical problem by offering the multi-colored picture image recording device characterized by having the control means which controls a cooling means or a press means.

[0015] Hereafter, this invention is explained concretely. The example of 1 configuration of the reversible record medium which can be used for drawing 1 with the approach and equipment of this invention is shown. On a support substrate, a heat-sensitive recording layer with the cholesteric-liquid-crystal nature compound of thermotropic nature and a transparent surface substrate are formed. Moreover, for the object of the improvement in a stacking tendency of liquid crystal, or the adhesive improvement between layers, a substrate layer and an interlayer may be prepared between each substrate and a heat-sensitive recording layer.

[0016] As a support substrate, plastic films, such as PET, PC, and PES, or these complex, a glass plate, etc. can be used, for example. 50-500 micrometers of thickness of the support substrate in the case of considering as a reversible sheet-like record medium are usually preferably set to about 100-300 micrometers. When considering as other display units, the tabular rigid body is sufficient, and especially the thickness of a base material is not limited. As an optical absorption layer for observing a cholesteric reflected color, what applied the black coating etc. to the rear-face side of a support substrate, and the thing by which the black pigment was distributed in the aforementioned support substrate are used.

[0017] Although plastic films, such as PES, PEI, etc. which are excellent in transparency and thermal resistance, are desirable as a surface substrate, it is not limited to these. When recording with contact process heating apparatus like a thermal head from the front-face side of a record medium, the thickness of a surface substrate has 1 micrometer - desirable about 30 micrometers. If thicker [ if thin less than / this / , a mechanical strength will be insufficient and breakage of a substrate will arise, and ] than this, the heat transfer effectiveness to a heat-sensitive recording layer gets worse and is not desirable.

[0018] the thermostat which there is memory nature and can fix a cholesteric-liquid-crystal phase as a heat-sensitive recording layer -- fatty tuna -- all are usable if the big liquid crystallinity compound is included. For example, side-chain mold macromolecule cholesteric liquid crystal can be used. For example, all are usable if it is the polymer liquid crystal in which selective reflection which is indicated

by aforementioned JP,4-174415,A, aforementioned JP,6-273707,A, etc. is shown.

[0019] The weight average molecular weight of a macromolecule cholesteric-liquid-crystal compound has the desirable range of 10,000 to 500,000. It is not desirable in order for record and elimination to take several hours, if larger [ if smaller than 10,000, the preservation stability of a record condition will worsen, and ] than 500,000. Generally, by the macromolecule cholesteric-liquid-crystal system, there is a problem that chart lasting time and blanking time become comparatively long.

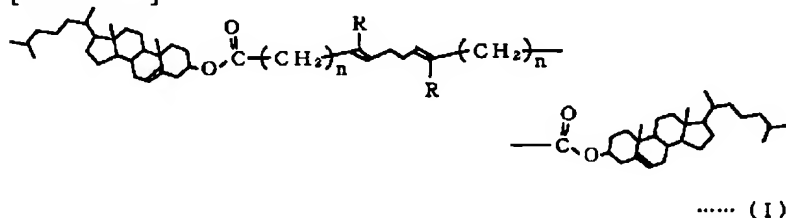
[0020] Moreover, when T<sub>g</sub> is low, the preservation stability of the recorded fixed condition may get worse, and a fixed condition may disappear by preservation under the temperature which is room temperature extent. Therefore, as for T<sub>g</sub>, it is desirable that it is at least 30 degrees C or more. However, when dealing with the record medium and equipment of this invention only under a low-temperature environment, especially T<sub>g</sub> should just be beyond the temperature of the environment which it is not limited but is dealt with.

[0021] Especially the thing for which the cholesteric-liquid-crystal nature compound in which molecular weight does not have molecular weight distribution preferably 10,000 or less [ 900 or more ] in this invention 2000 or less [ 1000 or more ] for the improvement in a recording rate, or its mixture (inside molecule cholesteric liquid crystal) is used is desirable. Moreover, when glass transition temperature is observed, as for said inside molecule cholesteric liquid crystal, it is desirable that it is 30 degrees C or more.

[0022] As a cholesteric-liquid-crystal compound which has the above properties, what is shown, for example in the following type (I) and (II) is mentioned.

[0023]

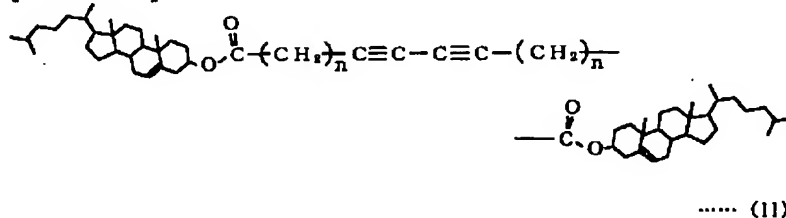
[Formula 3]



(The inside of a formula, n= 5, 6 and 7 and R=H, CH<sub>3</sub>)

[0024]

[Formula 4]



(The inside of a formula, n= 2, 3, 4, 5, 6, 7, 8, 9, 10)

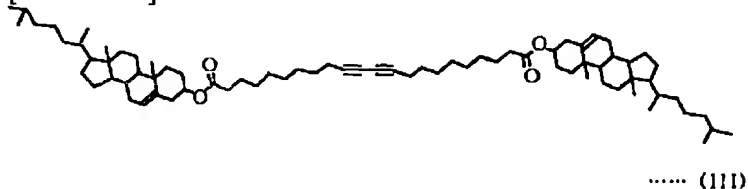
The molecular weight is 2000 or less, and glass transition temperature is 30 degrees C or more, and the cholesteric-liquid-crystal compound used as a liquid crystal record ingredient indicated to be a before type (I) by (II) shows a cholesteric-liquid-crystal phase above glass transition temperature, and shows an isotropic phase at the temperature beyond it further. Moreover, you may be the mixture with which the number of n differs also from the compound shown by the before type (I) and (II), respectively, and may be a before type (I) and the mixture of (II) further.

[0025] Since the stability by the cholesteric pitch reflected color by which the cholesteric liquid crystal (Dicholesteryl 10, 12-Docosadienedioate: henceforth C8DY8C) shown by the bottom formula (III) especially whose n of a before type (II) is 8 was fixed is high, it is desirable. The

cholesteric-liquid-crystal compound used by this invention may mix two or more of the kinds, and may be used.

[0026]

[Formula 5]



[0027] Phase change model drawing of an inside molecule cholesteric-liquid-crystal nature compound is shown in drawing 8 . If it heats from the crystal phase, it will become an isotropic phase above the melting point. When it cools slowly or quenches to the temperature which shows a cholesteric-liquid-crystal phase from there, the selective reflection color according to temperature is shown. Here, the about 100-degree C thing for which an elevated temperature shows a cholesteric-liquid-crystal phase comparatively is desirable. If it cools slowly from a cholesteric-liquid-crystal phase to room temperature extent, it crystallizes and will be in the nebula condition by light scattering. At this time, when a record layer is thin, it may be mostly observed as transparency.

[0028] If it quenches from a cholesteric-liquid-crystal phase to room temperature extent, it will become a vitrified solid-state (cholesteric glass phase) holding the spiral molecular arrangement of a cholesteric-liquid-crystal phase, and the selective reflection color depending on a spiral pitch will be observed. By setting the temperature of the heat-sensitive recording layer at the time of quenching initiation or a cooling rate, and its field as arbitration, the image in which the selective reflection color of arbitration is shown can record reversibly. If molecular weight is smaller than 900 here, on quenching conditions, crystallization takes place and a cholesteric glass phase is not fixed, either. Since the reorientation of the molecule accompanying quenching is early, this is considered. Moreover, if molecular weight is larger than 10,000, the practical record and practical elimination below hundreds ms extent will become [ 1 pixel ] difficult. moreover, a KORESURI tech glass phase -- about 100 degrees C -- it will crystallize and become cloudy if it heats to an elevated temperature comparatively. However, depending on an ingredient, it may transfer to a liquid crystal phase directly from a KORESURI tech glass phase.

[0029] What is necessary is just to choose preferably 0.5-50 micrometers of thickness of a heat-sensitive recording layer from the range of 1-20 micrometers suitably. Since the reflection factor in the wavelength from which the maximum echo is obtained will become low if a heat-sensitive recording layer is too thin, the contrast of a display image falls, if too thick, the optical absorption in a heat-sensitive recording layer will increase, and the contrast of a display image falls.

[0030] In addition, although it is desirable to \*\*\*\*\* only the liquid crystallinity compound in which selective reflection is shown as for a heat-sensitive recording layer, it may contain binder resin and a spacer particle. As binder resin, a polyvinyl chloride, polyvinyl acetate, an epoxy resin, phenoxy resin, acrylic resin, polyurethane, polyester, etc. are mentioned, for example. What is used for common liquid crystal displays as a spacer particle can be used.

[0031] It is desirable to usually exist in an about 400-700-micrometer light field, and, as for selective reflection wavelength, it can check human being by looking in this case. However, when reading with a machine, selective reflection wavelength may be \*\*\*\*(ing) to the ultraviolet region or the infrared region.

[0032] The example of 1 configuration of the equipment which embodies the approach of this invention to drawing 3 is shown. The reversible record medium itself is moved with the conveyance means which faced across the edge of a reversible sheet-like record medium. First, a red image is

recorded on the heat-sensitive recording layer of a reversible record medium as first selective reflection color. At this time, there are two kinds of approaches as follows among the approaches of recording the selective reflection color of arbitration.

1. Heat the Records Department using a heating means more than isotropic phase transition temperature, quench a liquid crystal phase at a stretch to room temperature extent with other cooling means, and fix the KORESURI tech glass phase which shows a desired selective reflection color, after cooling promptly to the liquid crystal phase which shows a desired selective reflection color from the temperature of an isotropic phase with a cooling means. Generally, in order to show a short wavelength color by the elevated-temperature side and for the KORESURI tech liquid crystal phase of thermotropic nature to record blue, quenching from an elevated-temperature condition is comparatively needed.

[0033] 2. Heat the Records Department using a heating means more than isotropic phase transition temperature, quench by the single step from the temperature of an isotropic phase to room temperature extent with a cooling means, and fix the cholesteric glass phase which shows a desired selective reflection color as a result. By adjusting the output of a heating means, and the temperature of a cooling means, a quenching rate is controllable. if a quenching rate is large -- blue -- red will be recorded if small.

[0034] if thrust is applied to the Records Department with an application-of-pressure means like drawing 4 before the temperature of the Records Department cools down until comparable with ambient temperature after recording a red image first by one of approaches, the red image of the pressurized part will change blue. here, before the temperature of the Records Department cools down until comparable with ambient temperature, when the cholesteric glass phase of the Records Department has a certain amount of temperature and thrust is impressed, a color change phenomenon or the happening temperature is said. Usually, said temperature is in the condition that the temperature of the record part after record actuation was cooled to about 40 degrees C - about 60 degrees C. However, since the above-mentioned temperature requirement changes with thermal recording ingredients to be used, especially a numeric value is not limited to said temperature requirement. Therefore, since what is necessary is just in the condition that the temperature of the record part after record actuation was cooled to about 40 degrees C - about 60 degrees C as mentioned above, even if it does not realize a big quenching rate in the approach of the above 1 or 2, a blue record image can be obtained eventually.

[0035] By the approach using the aforementioned application-of-pressure means, since it is easy to pressurize a comparatively large area and a band-like part by using a member like a roller as an application-of-pressure means at homogeneity, when it seems that the whole surface or the band-like part of a red image is changed blue, it is suitable.

[0036] In drawing 3 , although the thermal head was used as a heating means, in addition if it is a means with the capacity that the temperature of a heat-sensitive recording layer can be heated to more than isotropic phase transition temperature, the heating means of arbitration can be used. for example, an air heater, a heating roller, and a hot plate -- a laser beam -- \*\* -- \*\*\*\*\* is not limited to these heating means.

[0037] In drawing 3 , although the blower fan was used as a cooling means, if it is the matter and a member with the capacity to contact the record medium immediately after heating and to make it radiate heat, the cooling means of arbitration can be used. For example, although air, water, water, a metal member, the blower fan for they-cooling, a Peltier device, etc. are mentioned, it is not limited to these cooling means. the case where thermal head equipment is generally used -- the base material of the head, the air of an ambient atmosphere, and the support substrate of a record medium -- the very thing -- \*\* -- since it becomes a \*\*\*\*\* means, it becomes the quenching conditions by the single step of said approach of 2. moreover -- if two or more hot plates, heating rollers, etc. are used -- 2 of said 1 -- also realizing gradual quenching conditions -- \*\*\*\*\*.



[0038] As an application-of-pressure means, although the rubber roller of a couple was used, the member of the shape of the shape of a roller pressed against a record medium by the flat spring, a spring, etc. and a rod etc. is used. In the case of a roller-like member, it is forming a revolution drive etc., and it can also be operated as a part of conveyance means of a record medium. Furthermore, the heating means of contact molds, such as a heating roller and a thermal head, can also be made to use also [ means / application-of-pressure ].

[0039] Moreover, generally, the spring is installed in the die-length direction and the thermal head etc. is forced on the roller which counters a thermal head with this spring in many cases. Therefore, the thrust of the thermal head as an application-of-pressure means can be adjusted by changing the number and strength of said spring. The location and timing of an application-of-pressure means are suitably set up according to the cooling condition of the heat-sensitive recording layer after record.

[0040] Actuation of the aforementioned conveyance means, a heating means, a cooling means, and an application-of-pressure means may be controlled by the control means, for example, the control means which consists of a microcomputer. moreover, as a press means of an image, for example by the nib-like member, it may pressurize directly and you may inside draw. however, except when pressurizing directly and inside drawing by the nib-like member, in order to control welding pressure finely in a field generally, a complicated device is required for an application-of-pressure means, and it is difficult. That is, it is comparatively difficult to change only a minute part blue as a machinery by the above mechanical approaches.

[0041] After recording a with a red [ first ] image (image of the first selective reflection color) first like drawing 5 , the image (image of the second selective reflection color) of the red of another two-times eye is recorded there. Next, the first image passes beyond predetermined time amount since record, it is the whole surface of a heat-sensitive recording layer, or applying thrust selectively, and blue (image of the second selective reflection color) can be made to carry out color change only of the red image of a two-times eye in the condition that will be in the condition of not carrying out color change, and the image of a two-times eye carries out color change within predetermined time from record. It is also possible to change only a minute part which records a blue alphabetic character image into a red solid image by this approach blue. Moreover, if green and the color of a two-times eye are made into red for the first image, thrust is impressed selectively for example, and it blue-izes red [ a part of ], a multi-colored picture image in three primary colors can be recorded comparatively easily. In addition, in this invention, even if it is the record image of not only the first two-times eye but the third henceforth, color conversion of the record image by thrust is included, also when the color conversion of this image can be carried out by thrust.

[0042] As equipment, the same configuration as drawing 3 is possible, the application-of-pressure means is canceled, and after recording the first red image, a record medium is returned to an early location with a conveyance means. Then, it is made to halt so that the above-mentioned predetermined time may be satisfied. Next, when recording the second red image, an application-of-pressure means is operated and conversion actuation to the blue of the second red image is performed in a series of moving trucking of a record medium. Actuation of the aforementioned conveyance means, a heating means, and a cooling means application-of-pressure means is controlled by the control means, for example, the control means which consists of a microcomputer.

[0043] ambient temperature since the aforementioned approach uses the remaining heat which the record image section has after record actuation -- \*\* -- there is a problem of being easy to be influenced. Color change only of the part which reheated by reheating to temperature lower than the temperature which a cholesteric glass phase transfers to a liquid crystal phase or a crystal phase with the heating means of \*\* a second while recording the images of the first red also including the image which should be changed eventually and blue like drawing 6 there and then applying thrust within predetermined time in a heat-sensitive recording layer can be carried out blue. At the temperature of this reheating extent, since the usual record cannot be performed, no parts on which the first red image

is not recorded change. It can be stabilized and a color change phenomenon can be made to discover by controlling temperature required for a color change phenomenon by this approach positively.

[0044] Moreover, the thermal head equipment which is the first heating means as the second heating means and application-of-pressure means like drawing 7 can also be made to serve a double purpose. In this case, although the count of a round trip of a reversible record medium increases, an application-of-pressure roller etc. is omissible. Moreover, it is necessary to perform conveyance position control of a record medium to accuracy so that location gap of the first red image part and a reheating part may not arise. Moreover, if the part corresponding to an image somewhat thicker than the original red image is reheated, even if slight location gap will occur, a blue image uniform to the edge section is obtained. At the temperature of this reheating extent, since the usual record cannot be performed, image \*\*\*\* of an alphabetic character etc. is not generated.

[0045] In the image recording approach of this invention, when the storage temperature of the heat-sensitive recording layer after record is high, a color change phenomenon stops being discovered for a short time, and if storage temperature is low, a color change phenomenon will be comparatively discovered to long duration. Although storage temperature and the relation of predetermined time are not limited especially since they change with the class of ingredient, or presentations, they can perform positive color change actuation by carrying out color change actuation to proper timing in consideration of the predetermined time according to storage temperature.

[0046] Moreover, it asks for the storage temperature after record, and the relation of predetermined time experimentally from the record ingredient used beforehand, and even when environmental temperature changes by establishing a means to measure the temperature of the heat-sensitive recording layer after record and storage temperature changes, initiation timing of operation, such as the aforementioned second heating means, an aforementioned application-of-pressure means, etc. for performing color change actuation, can be controlled the optimal.

[0047] With above approach and equipment, although thrust was set constant, in this invention, the color of the selective reflection color after color change is changeable also by changing the magnitude of the thrust applied to an image. For example, red is also convertible green by adjusting thrust comparatively small. However, since it will become easy to generate the color nonuniformity by application-of-pressure nonuniformity if thrust is made small, it is desirable to lessen irregularity of the front face of a record medium or an application-of-pressure means. Moreover, it is desirable to optimize the surface hardness of an application-of-pressure means.